

## APPLICATION OF POWDERED BUILDING WASTES IN ADSORPTION TECHNOLOGIES

<sup>1</sup>Barbora DOUŠOVÁ, <sup>2</sup>Pavel REITERMAN, <sup>1</sup>Miloslav LHOTKA, <sup>2</sup>Martin KEPPERT,  
<sup>1</sup>David KOLOUŠEK

<sup>1</sup>University of Chemistry and Technology Prague, Czech Republic, EU,  
[dousovab@vscht.cz](mailto:dousovab@vscht.cz)

<sup>2</sup> Faculty of Civil Engineering, Czech Technical University in Prague, Czech Republic, EU,  
[pavel.reiterman@fsv.cvut.cz](mailto:pavel.reiterman@fsv.cvut.cz)

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### Abstract

Two powdered wastes originating in building materials production (waste brick dust (WBD) from the production of ceramic blocks and concrete slurry waste (CSW) from prestressed poles production used also in Fe-modified form (CSW<sub>Fe</sub>)) were studied as potential adsorbents of ecologically risk cations (Cd<sup>2+</sup>, Pb<sup>2+</sup>) and anions (As<sup>V</sup> as AsO<sub>4</sub><sup>3-</sup> and Cr<sup>VI</sup> as CrO<sub>4</sub><sup>2-</sup>) from contaminated waters. The WBD indicated very good adsorption selectivity for Cd<sup>2+</sup>, Pb<sup>2+</sup> and As<sup>V</sup> at a high adsorption efficiency (>90 %), and worse parameters for Cr<sup>VI</sup> adsorption (<30 % adsorption efficiency). The sorbent consumption was low (<70 - 100 g per 1 g of contaminant) for cations (Cd<sup>2+</sup>, Pb<sup>2+</sup>) and more than four times higher for As<sup>V</sup>. The adsorption of Cr<sup>VI</sup> on WBD was ineffective. The adsorption of cations (Pb<sup>2+</sup> and Cd<sup>2+</sup>) on CSW and anions (AsO<sub>4</sub><sup>3-</sup> and CrO<sub>4</sub><sup>2-</sup>) on CSW<sub>Fe</sub> ran in the same manner as on WBD. Fe-modification of CSW to CSW<sub>Fe</sub> increased its adsorption efficiency to anions by 15. - 20 %. The cations (Pb<sup>2+</sup>, Cd<sup>2+</sup>) were adsorbed almost quantitatively (≈100%) on the initial CSW at the sorbent consumption of 10 - 120 g per 1 g of contaminant. The adsorption of anions (As<sup>V</sup>, Cr<sup>VI</sup>) on CSW<sub>Fe</sub> reached >95% for As<sup>V</sup> and 40 - 60% for Cr<sup>VI</sup>, at the sorbent consumption of 80 - 200 g per 1 g of contaminant.

**Keywords:** Building waste, adsorption, heavy metals, toxic anions

### 1. INTRODUCTION

A secondary use of building waste has got into increased professional concern due to the growing development and production of building materials. The powdered waste brick dust (WBD), which arised at the production of ceramic blocks, is usually recycled in concrete production [1], or, in specific cases, it can be also applied as pozzolanic component of cement based materials to reducing the Portland cement consumption [2]. The annual production of Portland cement exceeds 4000 Mt [3,4] and is still rising. According to e.g. Damptoft er al. [5], the energy-intensive production of Portland cement .is responsible for about 5 % of global anthropogenic emissions of CO<sub>2</sub>, which initiated the development of new technologies primarily focused on recycling and secondary use of waste building products [6,7]. Fortunately, the powdered building wastes including WBD and CSW represent promising materials due to availability, low cost and appropriate properties. The chemical stability, environmental safety issues and silicate-like behavior determine their potential application as selective adsorbents in decontamination technologies [6,8].

In natural adsorption systems the sorbent selectivity has been primarily controlled by the pH of zero point of charge (pH<sub>ZPC</sub>) [9]. The solids with a low pH<sub>ZPC</sub> (aluminosilicates, quartz) attract mostly cations, while a high pH<sub>ZPC</sub> is typical for anion-active sorbents (Fe/Al oxides, gibbsite) [10,11]. The surface of mixed materials (soils, sediments, brick dust, slurries) mostly consists of diverse active sites, and the pH<sub>ZPC</sub> corresponds more or less to the median of all particular components. Therefore, they can behave as both cation-active and anion-active adsorbents with respect to current conditions.

The aim of this work was to study the sorption properties of WBD and CSW in initial and Fe-modified form on heavy metal cations (Pb<sup>2+</sup> and Cd<sup>2+</sup>) and toxic oxyanions (As<sup>V</sup> as AsO<sub>4</sub><sup>3-</sup> and Cr<sup>VI</sup> as CrO<sub>4</sub><sup>2-</sup>). The optimal

adsorption parameters were investigated in model water systems and calculated according to the Langmuir model.

## 2. EXPERIMENTAL PART

### 2.1. Used sorbents

The WBD is generated as a waste (grinding dust) during the production of vertically perforated ceramic blocks intended for thin joint masonry, while a sedimented CSW containing cement, mineral additives, fine fillers, admixtures and water, remains after the partial recycling of fresh concrete waste (1-4 wt.% of total concrete production). The elementary chemical composition, mineralogy and surface properties are given in **Table 1**.

**Table 1** Characterization of WBD and CSW

sample	chemical composition (wt%)						mineralogical composition	S <sub>BET</sub> (m <sup>2</sup> /g)	pH <sub>ZPC</sub>
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO			
WBD	49.5	19.7	6.1	0.8	13.5	4.8	illite, feldspar, quartz, micas, hematite	3.3	4.9
CSW	32.3	6.6	1.3	<0.1	46.9	1.8	muscovite, portlandite,	38.2	10.3
CSW <sub>Fe<sup>+</sup></sub>	26.6	4.3	29.8	0.4	18.7	2.1	calcite, quartz, (hornblende)	118.2	7.5

\*) surface modification with Fe<sup>2+</sup>

### 2.2. Model solutions

Model solutions of Pb<sup>2+</sup>, Cd<sup>2+</sup>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> were prepared from inorganic salts (PbCl<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, KH<sub>2</sub>AsO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> of analytical grade and distilled water, in the concentrations of 0.1 and 0.5 mmol.L<sup>-1</sup> and the natural pH (i.e. pH ≈ 3.5 for cationic solutions and pH 5-6 for anionic solutions). The concentration range was selected as appropriate for the simulation of a slightly increased amount of the contaminant in a water system to a heavily contaminated solution.

### 2.3. Fe-modification

The suspension of CSW (20 g) in 0.6M FeSO<sub>4</sub>·7H<sub>2</sub>O (1 L) was shaken in a sealed polyethylene bottle at laboratory temperature (20 °C) for 24 h. Then the solid phase was filtered off, washed with distilled water, dried at 60 °C, and homogenized [12]. Only a tiny surface layer of available Fe ions in reactive form is sufficient for the adsorption of oxyanions on the active surface sites of bulk oxo(hydroxides) [13].

### 2.4. Adsorption process

In adsorption experiments the cations (Cd<sup>2+</sup>, Pb<sup>2+</sup>) were adsorbed on the WBD and CSW, whereas the anions (As<sup>V</sup>, Cr<sup>VI</sup>) were adsorbed on the WBD and Fe-modified CSW<sub>Fe</sub>.

The suspension of model solution (50 mL) and defined dosage (0.5-15 g L<sup>-1</sup> of WBD and 1-20 g L<sup>-1</sup> of CSW or CSW<sub>Fe</sub>) was agitated in a batch manner at laboratory temperature (20 °C) for 24 hours [13]. The product was filtered off, and the filtrate was analysed for residual concentration of cations or anions. All adsorption data were fitted to the Langmuir isotherm [14,15] as the suitable and widely used adsorption model for natural sorbents, including oxides, aluminosilicates and soils.

## 2.5. Analytical methods

*Powder X-ray diffraction (XRD)* was performed with a Seifert XRD 3000P diffractometer with  $\text{CoK}\alpha$  radiation ( $\lambda = 0.179026$  nm, graphite monochromator, goniometer with Bragg-Brentano geometry) in the  $2\theta$  range of  $5 - 60^\circ$  with a step size of  $0.05^\circ 2\theta$ .

*X-ray fluorescence (XRF)* analyses of the solid phase were determined with an ARL 9400 XP+ spectrometer with a voltage of 20 - 60 kV, probe current of 40-80 mA and effective area of  $490.6 \text{ mm}^2$ . UniQuant software was used for data evaluation.

*The specific surface area ( $S_{\text{BET}}$ )* was measured on a Micromeritics ASAP 2020 (accelerated surface area and porosimetry) analyzer using the gas sorption technique. The ASAP 2020 model assesses single and multipoint BET surface area, Langmuir surface area, Temkin and Freundlich isotherm analysis, pore volume and pore area distributions in the micro- and macro-pore ranges by the BJH method. The micro-pore option used the Horvath-Kavazoe method, with  $\text{N}_2$  as the analysis adsorptive and an analysis bath temperature of  $-195.8^\circ \text{C}$ . The samples were degassed at 313 K for 1000 minutes.

*The concentration of Pb and Cd* in aqueous solutions was determined by atomic absorption spectrometry (AAS) using a SpectrAA-880 VGA 77 unit (Varian) in flame mode. An accuracy of AAS analyses was guaranteed by the Laboratory of Atomic Absorption Spectrometry of UCT Prague, CR, with the detection limit of  $0.5 \mu\text{g}\cdot\text{L}^{-1}$ , with a standard deviation ranging from 5 - 10 % of the mean.

*The concentration of As* in aqueous solutions was determined by Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) using a PSA 10.055 Millennium Excalibur apparatus. The samples were pre-treated with a solution of HCl (As-free, 36 % v/w) and KI (50 %) with ascorbic acid (10 %). The instrumental parameters included ppm and ppb modes, HCl (12 %) with KI + ascorbic acid solution as the reagent blank and 7%  $\text{NaBH}_4$  in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH as the reductant. The declared detection limit was 0.05 ppm and the standard deviation was experimentally determined as 2.5 %.

*The concentration of Cr* as  $\text{Cr}_2\text{O}_7^{2-}$  in aqueous solutions was measured with a UV/VIS spectrophotometer (Evolution 220, Thermo Fisher Scientific) at 350 nm following acidification with  $\text{H}_2\text{SO}_4$  (10%wt.) [16]. The verified detection limit was  $50 \mu\text{g}\cdot\text{L}^{-1}$  and the experimentally determined standard deviation was less than 5 %.

## 3. RESULTS AND DISCUSSION

### 3.1. Adsorption capacities (Langmuir model)

The theoretical adsorption capacities  $Q_t$  calculated according to the Langmuir model (**Figure 1**) indicated a higher adsorption affinity of cations ( $\text{Cd}^{2+} > \text{Pb}^{2+}$ ) to WBD, and significantly better adsorption of oxyanions ( $\text{AsO}_4^{3-} > \text{CrO}_4^{2-}$ ) to  $\text{CSW}_{\text{Fe}}$ . These results corresponded well to the previous studies of Doušová et al. [6,13] supporting the theory of inner-sphere surface complexation for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{AsO}_4^{3-}$  adsorption, and both outer- and inner-sphere complexation with prevailed weaker monodentate forms for  $\text{CrO}_4^{2-}$  [17]. Relatively different  $Q_t$  values resulted from the distinct structural and binding properties (size, charge distribution, binding energy etc.) of tested ions.

### 3.2. Adsorption efficiency

The efficiency of adsorption process represents very important characteristic of adsorbent-adsorbate system. According to the percentage adsorption efficiencies (**Figure 2**),  $\text{Pb}^{2+}$  and  $\text{As}^{\text{V}}$  were selectively adsorbed (75-99%) on all sorbents. The  $\text{Cd}^{2+}$  was almost quantitatively adsorbed on cation-active adsorbents (WBD and CSW), at the ineffective adsorption on anion-active  $\text{CSW}_{\text{Fe}}$ . This phenomenon was in agreement with the expected mechanism of cation adsorption [6,9]. A generally worse adsorption of  $\text{Cr}^{\text{VI}}$  associated with low

adsorption efficiency resulted from a lower adsorption energy of Cr<sup>VI</sup> oxyanions and their tendency to the electrostatic binding via outer-sphere surface complexes [18].

The highly alkaline WBD and CSW adsorption environment provided the formation of insoluble surface precipitates and polynuclear complexes, which could also improve the adsorption yield [19].

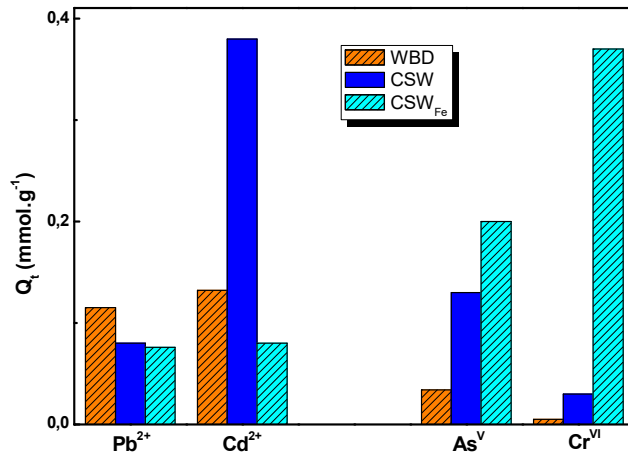


Figure 1 Langmuir theoretical adsorption capacities  $Q_t$

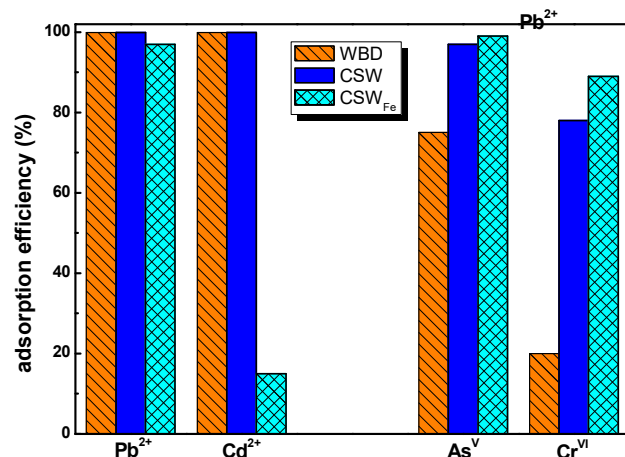


Figure 2 Percentage efficiency of adsorption processes

### 3.3. Sorbent consumption

According to obtained data, a hypothetical sorbent consumption for the removal of 1 g of toxic element was calculated for better estimation of its possible use in decontamination technologies (Figure 3).

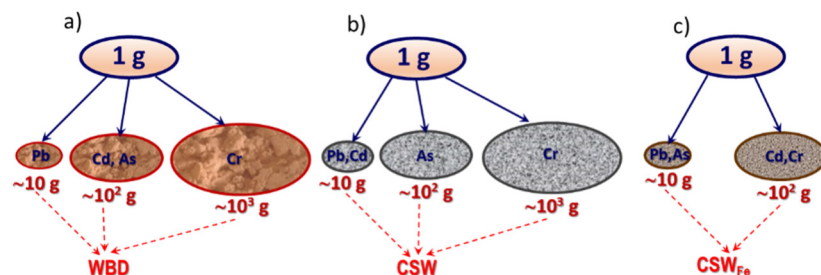


Figure 3 Sorbent consumption per 1 g of toxic element; a) WBD, b) CSW, c) CSW<sub>Fe</sub>

As shown in the scheme (**Figure 3**), all adsorbents were perspective for  $Pb^{2+}$  removal at a low sorbent consumption (in tens of g per 1 g of Pb). In the case of  $Pb^{2+}$  the participation of predicted poorly soluble  $Pb(OH)_2$  clusters, which substantially increased the adsorption yields, should be considered [8]. The both cation-active adsorbents (WBD and CSW) were also promising for  $Cd^{2+}$  adsorption, particularly CSW.

According to the excellent adsorption properties of arsenates associated with the inner-sphere surface complexation [13,17],  $As^V$  was selectively adsorbed on anion-active  $CSW_{Fe}$  at a low sorbent consumption (in tens of g per 1 g of As), and also effectively (>75 %) but at a higher sorbent consumption (in hundreds of g per 1 g of As) to the both WBD and CSW. From the sorbents tested, only  $CSW_{Fe}$  appeared to be perspective for  $Cr^{VI}$  removal at a sorbent consumption in hundreds of g per 1 g of Cr. For tested ions, the potential use of building wastes in decontamination technologies decreased in the order:  $Pb^{2+} > Cd^{2+} \approx As^V > Cr^{VI}$ .

#### 4. CONCLUSION

Powdered building wastes (WBD and CSW) can be used as selective sorbents of cationic and anionic contaminants at the adsorption efficiency more than 75 %. The  $pH_{ZPC}$  values of sorbents indicate the predicted affinity of adsorbed cations or anions, but a highly alkaline system promoting the formation of surface precipitations and clusters can cause the deviation from usual adsorption behaviour. The CSW appears to be even better adsorbent compare to the WBD and its surface modification with  $Fe^{2+}$  improved the selectivity to anionic contaminants. The utilization of tested sorbents to remove toxic ions from contaminated water decreased in the order:  $Pb^{2+} > Cd^{2+} \approx As^V > Cr^{VI}$ . Lead as  $Pb^{2+}$  was selectively adsorbed on all tested sorbents at the sorbent consumption in tens of g per 1 g of Pb. In this case, the formation of insoluble surface precipitation  $Pb(OH)_2$  and clusters  $Pb_4(OH)_4^{4+}/Pb_6(OH)_8^{4+}$  promoting the adsorption yield, could be considered. Cadmium as  $Cd^{2+}$  was similarly adsorbed on the CSW, and with a higher sorbent consumption (in hundreds g per 1 g of Cd) on the WBD. For  $As^V$  and  $Cr^{VI}$  removal,  $CSW_{Fe}$  was the most appropriate adsorbent with the sorbent consumption in tens of g per 1 g of As and hundreds of g per 1 g of Cr, respectively. Regardless of the sorbent consumption, the adsorption of  $Cd^{2+}$  on  $CSW_{Fe}$  and  $Cr^{VI}$  on WBD was completely ineffective.

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